Waste valorization in winemaking industry: Vine shoots as precursors to optimize sensory features in white wine

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ARTICLE INFO

ABSTRACT

Postharvest pruning generates large amounts of vine-shoots (VSs) that are used as a domestic fuel or burned in the field, resulting in the release of CO_2 and NO_2. Its use as a raw material for the preparation of activated carbons (ACs) turns VS into a high added-value product. In this work, ACs have been prepared from VS by physical and chemical activation. The discoloring and deodorant capacity of these ACs has been analyzed and correlated with their physicochemical characteristics. We have demonstrated the excellent features of ACs prepared from VS to be used as fining agents of wines. ACs have been employed to mitigate the negative effects of browning on a white wine commodity as well as to decrease the presence of unpleasant aromas (e.g., vinyl phenols), contributing to solve an actual problem in the winemaking industry. The suitability of ACs to be used in enology was tested on a white wine cv. Pardina. The physically activated samples exhibited a higher capacity to remove polyphenolic compounds and improved the chromatic characteristics. Principal Component Analysis (PCA) was applied to study the discoloring capacity of the samples and their ability to remove unpleasant aromas.

1. Introduction

Agrifood industries produce enormous amounts of by-products in diverse processes aiming at converting raw materials into final goods. For instance, the conditioning tasks of the vine (*Vitis vinifera*, L.) include major pruning tasks once the harvest is finished, with the subsequent generation of large amounts of VS waste that may pose a severe environmental problem if they are burned in the field, releasing CO_2 and NO_x. In Europe -and mainly in the Mediterranean countries-vast areas are devoted to the cultivation of the vine. Only in Spain, in 2019, there were 967,234 ha of vineyard. Considering an average of 2000 vines/ha, and a yield of shoots of 1.3 kg/vine (General Technical Secretariat, 2020), approximately 2.5 million tons of VSs would be available yearly in the Spanish vineyards. Thus, remarkable efforts have been made to valorize this bioresource. Some alternatives are pulping (Jiménez et al., 2009), energetic exploitation (Gañán et al., 2006; Mendívil et al., 2013),

extraction of organic chemical products (Bustos et al., 2007; Delgado-Torre et al., 2012), biosurfactants (Rodríguez-Pazo et al., 2013), antioxidants (Anastasiadi et al., 2012; Spatafora et al., 2013), antimicrobials (Dias et al., 2015), antifeedant and phytotoxic compounds (Sánchez-Gómez et al., 2016), fungicides and nutraceuticals (Guerrero et al., 2016) and as a source of nutrients for ruminants (Molina-Alcaide et al., 2008). Recently, VSs have also been tested as enological additive in winemaking (Cebrián-Tarancón et al., 2019) and as viticultural biostimulant (Sánchez-Gómez et al., 2017).

Activated carbon (AC) can be defined as a carbonaceous material that exhibits well-developed porosity and specific surface area. Increasing interest has arisen in connection with the preparation of ACs from a wide variety of wastes in general and agroindustrial residues in particular (Ioannidou & Zabaniotou, 2007). VSs exhibit high lignin contents (ca. 40%), thus being an excellent raw material for the preparation of ACs. Furthermore, after the recovery and extraction of most of

the aforesaid valuable chemicals, VSs residues remain mainly unaltered in terms of their lignocellulosic structure and can be further valorized in the form of ACs. Corcho-Corral et al. (2006) reported the preparation of ACs from VSs by chemical activation with H_3PO_4 at low temperatures. Such materials exhibit a well-developed specific surface area and porous structure. Also, some of the carbonaceous adsorbents prepared from VSs were successfully used by the referred authors in the treatment of Spanish white wines with the aim of significantly reducing its content of polyphenolic compounds that are responsible for browning and maderization processes (Corcho-Corral et al., 2005). It is well-known that AC is an excellent adsorbent of solutes. In the case of wine, which is a multi-component chemical system, its various components can be selectively adsorbed depending on the type of AC used, so that the quality and organoleptic properties of the wine can be controlled (Doulia et al., 2017) without negatively affecting the sensory quality of wine (Gava et al., 2020). The application of AC in the wine industry is hence particularly adequate (Parish et al., 2017a). The presence of undesired or potentially toxic compounds in wines can also by palliated with the aid of ACs. The wine commodities can become contaminated with mycotoxins produced by certain fungi (Oteiza et al., 2017). For instance, ochratoxin A (OTA, a product of fungal metabolism) poses a severe risk to human health and is considered as a potential carcinogen (Corrêa et al., 2022). The removal of OTA from wine by adsorption onto ACs has received a great deal of attention (Cosme et al., 2021; Ertan Anli et al., 2011; Espejo & Armada, 2009; Olivares-Marín et al., 2009). Also, geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol), a substance responsible for earthy off-flavor that is generated from the metabolism of *Penicillium expansum* fungus, has been removed from white wines by using ACs (Behr et al., 2013).

Due to its excellent adsorptive behavior, AC finds application not only in the treatment of wine but also of various products that are manufactured by the wine industry. Doses vary depending on the type and concentration of the target molecule to be removed (Parish et al., 2017b). For instance, discoloration of musts and concentrated musts is achieved at doses of 50–100 g/hL or 100–200 g/hL, respectively. White wine can also be discolored, and the straw-yellow and pinkish-yellow hues can be adequately modified. In the elaboration of vermouth, AC is used for the treatment of the base wines but not of the finished product (Panesar et al., 2011). The doses used with such an aim can range from 50 up to 100 g/hL. In the manufacture of liquors and spirits, which must be frequently presented to the consumer perfectly colorless, AC is used to treat the sugar syrups that are part of the composition of many liquors. Finally, some kinds of vinegar are treated with activated carbon not only to obtain a clear liquid but also to remove organic impurities that can make the product cloudy and alter its smell and taste (López et al., 2003).

This work aims at investigating the preparation of ACs from VSs wastes by physical and chemical activation as well as to analyze their removal capacity of chromatic and aromatic compounds present in wine. Adsorbents that specifically remove the chromatic compounds responsible for browning while maintaining the aroma of the wine will be selected. This general purpose is in line with the circular economy principles, according to which this waste is re-injected into the production circuit as a secondary raw material and, eventually, gives rise to a new and valuable product.

2. Experimental

2.1. Material and reagents

In the present study, Cabernet-Sauvignon vine shoots (VS) from the post-harvest pruning of 2020 were kindly provided by a local vineyard sited in Tierra de Barros (Badajoz province, SW Spain). VS used as the raw material for the preparation of the ACs was firstly air-dried for several days and next crushed and sieved, and the size fraction below 4 mm was selected as the precursor.

All reagents used in this study were of analytical grade: NaCl, H_3PO_4, KOH, $ZnCl_2$, anhydrous sodium acetate, glacial acetic acid, and HCl were purchased from Panreac and 4,5-dimethylfurfural was purchased from Aldrich. All gases were of the maximum purity and were provided by Air Liquide.

A mono-varietal (i.e., single grape, cv. Pardina) white wine from the 2020 vintage was used in this study.

2.2. Preparation of the adsorbents

2.2.1. Physical activation method

The raw material (~10g of VS) was firstly carbonized at 600 or 900 °C in a furnace (heating rate 10 °C min^{-1}) under an inert N_2 atmosphere for 2 h. After cooling, the carbonized product was removed and weighed. In the second step of the physical activation, the carbonized sample was contacted with the activating agent (air, carbon dioxide or steam) under the operational conditions summarized in Table S1 (Supplementary material).

2.2.2. Chemical activation method

Firstly, the raw material (~25 g of VS) was contacted with 250 mL aqueous solution of the activating agent (AA, i.e., H_3PO_3, $ZnCl_2$, or KOH) with an impregnation ratio equal to 1g of AA per gram of VS. Impregnation was conducted at 85 °C under continuous stirring. Impregnation time was 2 h for H_3PO_4 and KOH, and 7 h for $ZnCl_2$. Both phases were separated by vacuum filtration and oven-dried (120 °C, 24 h). Next, the impregnated precursor (≈10 g) was thermally treated (heating rate 10 °C min^{-1}) under N_2 atmosphere (flow rate 80 mL min^{-1}). The isothermal treatment time was 2 h. Cooling to room temperature was made under N_2 atmosphere to prevent oxidation. After cooling, samples were thoroughly washed to remove the excess of AA. The ACs were oven-dried (120 °C, 12 h) and placed in tightly closed containers. Table S1 also lists the preparation conditions of the chemically activated samples.

2.3. Characterization of the adsorbents

2.3.1. Chemical composition, texture, and morphology

The elemental analysis (C, H, N, S) of the VS and the ACs was determined with the aid of a Leco CHNS-932 analyzer. Approximately 1 mg of sample was weighed and placed inside the furnace in an inert silver crucible and next combusted at 1000 °C under a constant oxygen flow (80 mL/min). This results in the formation of CO_2, H_2O, N_2, and SO_2. The weight percent of C, H, N, and S were determined by infrared detection of CO_2, H_2O, and SO_2, and by thermal conductivity of N_2, using He (>99.9% purity) as the carrier gas in all cases. The oxygen content was obtained by difference as %O = 100 – (%C + % H +%N + %S).

The textural characterization was carried out by gas adsorption, mercury porosimetry, and density measurements. The adsorption isotherms were performed using N_2 as the adsorbate at −196 °C in a Quantachrome Autosorb-1 equipment. Approximately 0.15 g of carbon was firstly degassed (250 °C, 12h, pressure below 10^{-3} Torr). The specific surface area (S_{BET}) was estimated using the BET method, and the micropore volume (W_0) was obtained by applying the Dubinin-Radushkevich equation.

A mercury porosimeter (Autoscan-60, Quantachrome) was used in the experiments of mercury intrusion for the determination of the mesopore (V_{me-p}) and macropore (V_{ma-p}) volumes. Approximately 0.15–0.20 g of sample was used. The mercury contact angle was 140°, and the surface tension was 480 erg cm^{-2}. Pressures between 20 and 6·10^4 psi (i.e., 0.10–414 MPa) were applied, which correspond to a pore diameter range comprised between 54,000 and 18 Å. As usual, mercury density (ρ_{Hg}, g·cm^{-3}) measurements were made while performing mercury porosimetry. The total pore volume (V_T) was calculated as $V_T = W_0 + V_{me-p} + V_{ma-p}$.

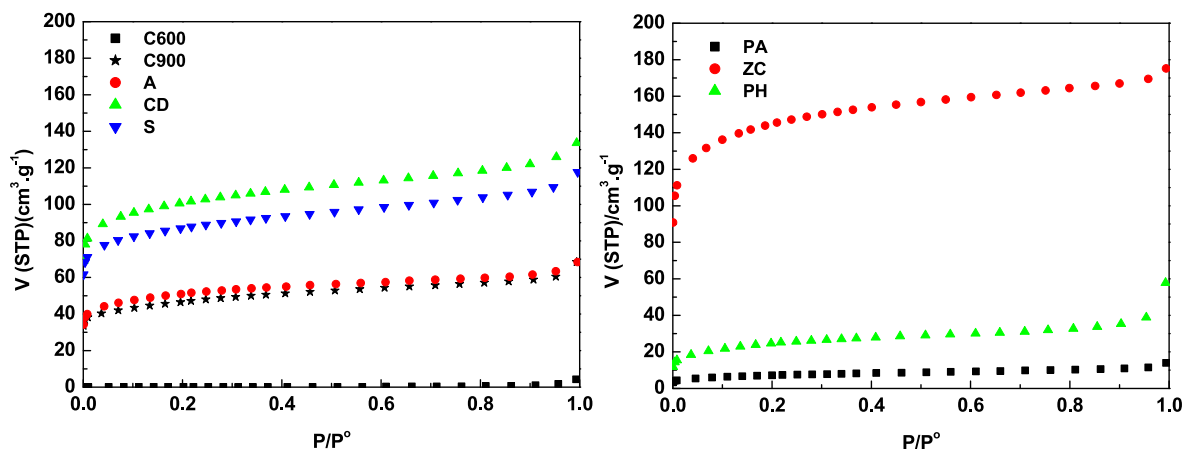SEM images of the samples were registered using a Quanta 3D FEG/

Fig. 1. N$_2$ adsorption isotherms at −196 °C of samples prepared by physical (left) and chemical (right) activation processes.

FEI Co scanning electron microscope.

2.3.2. Surface chemistry

FT-IR spectra were acquired using a PerkinElmer 1720 spectrophotometer in the range of wavenumbers 400–4000 cm^{-1} (2 cm^{-1} resolution). Fifty scans were registered for each record. Disks were prepared using KBr as a dispersing agent and binder in a sample-to-KBr proportion equal to 500:1.

Surface chemistry was also analyzed by determining the pH of the point of zero charge (pH$_{PZC}$). A method previously described elsewhere was used with such an aim (Mendoza-Carrasco et al., 2016).

2.4. Evaluation of the effect of the contact between wine and ACs

A monovarietal white wine (cv. Pardina) from the 2020 vintage, under the AOC Ribera del Guadiana (Extremadura, Spain), and not subjected to prior clarification and stabilization was used to analyze the effects of ACs on its sensory features. Conventional enological parameters of the wine (ethanol content v/v: 12.1%; pH: 3.3; titratable and volatile acidity: 4.5 g L^{-1} tartaric acid and 0.20 g L^{-1} acetic acid, respectively) were determined according to standardized OIV methods (International Organisation of Vine and Wine, 2018).

The evaluation of the effect of the contact between wine and ACs was carried out in two steps. Firstly, the discoloring capacity of ACs was determined by analyzing the phenolic substances and the chromatic characteristics of the wine before and after contact with AC. In the second phase, the effect on aromatic characteristics was evaluated by determination of the volatile composition and calculating the Odor Activity Value (OAV) of the wines. In this second phase, only the two ACs that showed the best discoloring activity were used.

A methodology previously reported by our research group (Corcho-Corral et al., 2005) was used to evaluate the discoloring and deodorizing capacity of the ACs. 100 mL of untreated wine (i.e., control wine, CW) were contacted under constant agitation with the AC for 48 h. After this time, the treated wine (TW) was separated from the adsorbent by centrifugation. All tests were performed in triplicate. AC doses of 0.25 and 0.50 g L^{-1} were used to analyze the possible incidence of the dose in the adsorption of substances.

2.4.1. Phenolic composition and chromatic characteristics

The phenolic composition and color were analyzed by spectrophotometry (Iland, 2004). Phenolic index (PI), Hydroxycinnamates (H), and Brown Pigments (BP) were estimated from the absorbance measurements (in absorbance units, AU) at the wavelengths of 280, 320, and 420 nm, respectively (i.e., A$_{280}$, A$_{320}$, and A$_{420}$, respectively). The content of hydroxycinnamates (H) was calculated as (A$_{320}$ - 1.4). Flavonoids (F) concentration was estimated as (PI-2/3H). Values of 7.58 AU for PI,

3.36 AU for H, 5.34 AU for F, and 0.27 AU for BP were obtained for the Pardina control wine.

The color definition was evaluated as CIE space, using the D65 illuminant and a 10° observer by the simplified method using the absorbances at 450, 520, 570 and 630 nm (Pérez-Caballero et al., 2003) and the data were processed with the MSCV (Simplified Wine Color Method) software. The vertical axis, L*, is a measure of lightness, from completely opaque (0) to completely transparent (100); a* is a measure of redness (or -a* of greenness), and b* of yellowness (or -b* of blueness). C* was calculated as [(a*)^2+(b*)^2]$^{0.5}$. C* is the quantitative attribute of colorfulness and indicates the contribution of a* (redness) and b* (yellowness) to the wine color. The values of L*, b* and C* for CW were 93.20, 23.96, and 22.97, respectively. The color difference (ΔE*ab) was defined as [(ΔL*)^2+(Δa*)^2+(Δb*)^2]$^{0.5}$ (Escudero-Gilete et al., 2010).

A UV-spectrophotometer PerkinElmer Lambda 3 B was used, with path lengths of the quartz cells equal to 1 cm for phenolic composition analysis and 2 mm for the color evaluation. All analyses were carried out in duplicate.

The variations of the phenolic index and chromatic parameters ie, VPI, VH, VF, VBP, VL*, Vb* and VC* were evaluated as V (%) = [(P$_{tw}$-P$_{cw}$)/P$_{cw}$] × 100, where P$_{tw}$ is the value of the parameter in the treated wines (namely, WC600, WC900, WA, WCD, WS, WPA, WZC, and WPH), and P$_{cw}$, the value of such parameter in the untreated wine (CW).

2.4.2. Volatile compounds analysis and odor activity value (OAV)

The volatile compounds were extracted as proposed by Coelho et al. (2020). In a 10 mL tube, 8 mL of wine, 2.4 µg of internal standard (4-nonanol), and a magnetic stir bar were placed. Sample was stirred with 400 µL of dichloromethane for 15 min at 18 °C. Tubes were placed vertically, and agitation was regulated in order to maintain dispersion of solvent micro-drops without reaching the sample surface. After cooling at 0 °C for 10 min, the magnetic stir bar was removed, and the organic phase was detached by centrifugation (RCF = 5118; time = 5 min; temperature = 4 °C). All the extractions of volatiles were made in triplicate.

Volatile compounds were analyzed using a GC-MS system comprising an Agilent Technologies 6890N gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) and an ion-trap mass spectrometer. A 1-µL injection was made into a capillary column, coated with CP-Wax 52 CB (inner diameter 50 × 0.25 mm, film thickness 0.2 µm; Chrompack). The temperature of the injector (model 7683) was programmed from 20 °C to 250 °C, at 180 °C·min^{-1}. The oven temperature was held at 40 °C for 5min and then risen from 40 °C to 250 °C, at 3 °C·min^{-1}, held for 20 min at 250 °C, and finally programmed to go from 250 °C to 255 °C at 1 °C·min^{-1}. The carrier gas was helium N60 (Air Liquide, Paris, France) at 103 kPa, which corresponds to a linear

Table 1
Elemental analysis, textural properties and pH$_{PZC}$ of the samples.

Elemental analysis									
	VS	**C600**	**C900**	**A**	**CD**	**S**	**PA**	**ZC**	**PH**
C	43.22	76.16	76.81	60.63	70.83	71.75	61.61	70.26	72.14
H	6.10	2.51	1.49	2.83	1.39	1.82	3.58	3.56	2.91
N	0.87	1.38	1.14	1.45	1.22	1.28	1.15	1.16	0.49
S	0.05	0.07	0.00	0.00	0.00	0.00	0.00	0.08	0.14
Textural properties									
		C600	**C900**	**A**	**CD**	**S**	**PA**	**ZC**	**PH**
S_{BET}/m^2 g^{-1}	N$_2$ adsorption	<1	143	154	300	260	23	435	78
W_0/cm$^3 \cdot$g^{-1}		0.00	0.09	0.09	0.17	0.15	0.01	0.25	0.05
V_{mi}/cm$^3 \cdot$g^{-1}		0.00	0.07	0.07	0.15	0.13	0.01	0.21	0.03
V_{me}/cm$^3 \cdot$g^{-1}		0.00	0.03	0.02	0.05	0.04	0.01	0.05	0.03
V_{me-p}/cm$^3 \cdot$g^{-1}	Mercury porosimetry	0.16	0.25	0.10	0.24	0.19	0.05	0.09	0.06
V_{ma-p}/cm$^3 \cdot$g^{-1}		0.78	0.68	0.82	0.57	0.71	0.46	0.17	0.57
ρ_{Hg}/g·cm^{-3}	Density measurements	0.52	0.65	0.48	0.71	0.77	0.69	0.74	0.53
V_T/cm$^3 \cdot$g^{-1}		0.94	1.02	1.01	0.98	1.05	0.52	0.51	0.68
pH$_{PZC}$									
		C600	**C900**	**A**	**CD**	**S**	**PA**	**ZC**	**PH**
pH$_{PZC}$		9.0	10.0	8.6	10.0	10.0	2.0	3.4	6.4

Key: S_{BET}: specific surface area; V_{mi}: micropore volume from N$_2$ adsorption data; V_{me}: mesopore from N$_2$ adsorption data; V_{me-p}: mesopore volume from mercury intrusion data; V_{ma-p}: macropore volume; ρ_{Hg}: mercury density; V_T: total pore volume. The textural data were obtained from the N$_2$ adsorption isotherms at −196 °C: S_{BET} ($P/P^0 = 0.05$–0.35, $a_m = 16.2$ Å^2), V_{mi} (volume adsorbed, V_{ad}, at $P/P^0 = 0.10$), and V_{me} (V_{ad} at $P/P^0 = 0.95 - V_{ad}$ at $P/P^0 = 0.10$); W_0 (Dubinin–Radushkevich equation); mercury intrusion curves: V_{me-p}, V_{ma-p}, and the mercury density values (ρ_{Hg}): $V_T = W_0 + V_{me-p} + V_{ma-p}$. V_{mi}, V_{me}, and W_0 are expressed as liquid volumes.

speed of 180 cm s^{-1} at 150 °C. Electronic impact mode (70 eV) was used, with acquisition range 29 < m/z < 360, and acquisition rate of 610 ms. Identification was performed using the Wsearch 32 free software. All the compounds were quantified as 4-nonanol equivalents. The odor activity value (OAV) was determined to evaluate the contribution of a chemical compound to the aroma. OAV indicates the importance of a specific compound in the odor of a sample and provides a quantification of its contribution to the odor of such a sample. It was calculated as the ratio between the concentration of an individual compound and the perception threshold found in the literature (Etiévant, 2017; Francis & Newton, 2005; Lu et al., 2020).

2.5. Data analysis

Differences between samples were compared using ANOVA and LSD test (95% probability). Principal component analysis (PCA) was performed using phenolic composition and color, and textural characteristics of ACs. The relationships between the phenolic index and textural characteristics of ACs were assessed by correlation analysis. These analyses were performed using XLSTAT Bases 2015 statistical package.

3. Results and discussion

3.1. Characterization of the raw material and the adsorbents

3.1.1. Texture and morphology

The N$_2$ adsorption isotherms at −196 °C of the carbonized precursors (namely, C600 and C900) and the physically activated samples are shown in Fig. 1, left. N$_2$ adsorption capacity is low for C900, and even more for C600, which suggests a scarce development of the micro- and mesoporosity, with incipient pores blocked because of the incomplete pyrolysis of the material.

The shape of the adsorption isotherms of physically activated samples corresponds to the Type 1 of the BDDT classification, albeit to a different extent depending on the activating agent used. Sample A (air) is an essentially microporous solid, whereas for samples CD (carbon dioxide) and S (steam) the larger adsorbed volume of N$_2$ suggest a more developed micro- and mesoporosity.

Fig. 1, right, depicts the adsorption isotherms of samples prepared by chemical activation namely, PA (H$_3$PO$_4$), ZC (ZnCl$_2$) and PH (KOH). Such isotherms also belong to the Type 1 of the BDDT classification. Sample ZC exhibits more developed microporosity, whereas PH is more mesoporous in nature as suggested by the increase of the volume of N$_2$ adsorbed at high values of P/P°. Values in Table 1 indicate that,
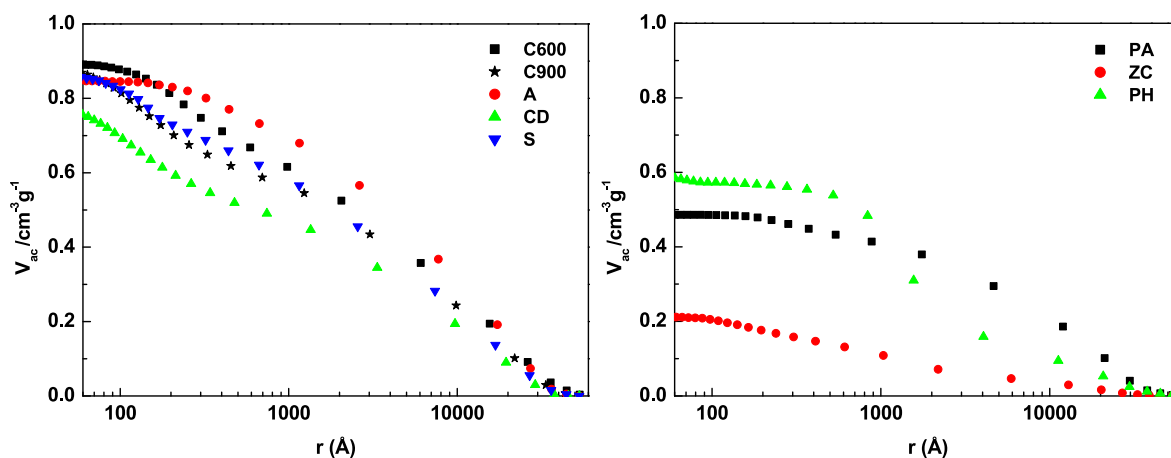

Fig. 2. Mercury intrusion curves of samples prepared by physical (left) and chemical (right) activation processes.
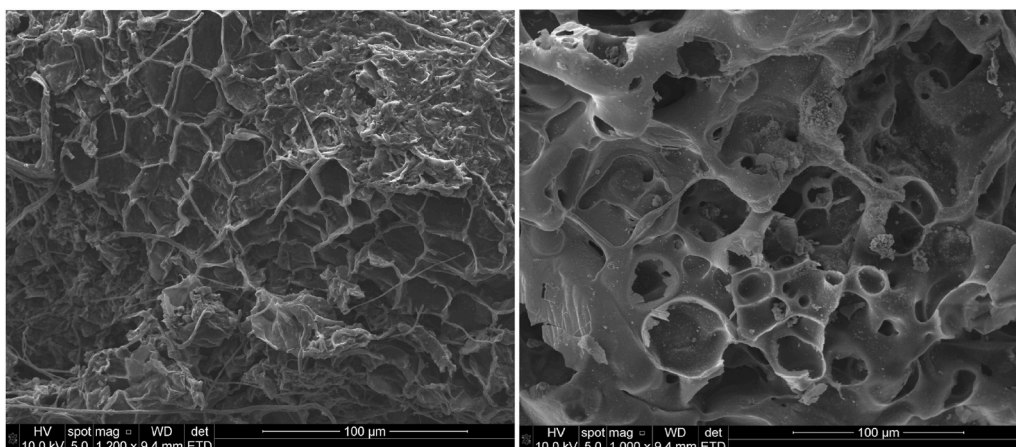
Fig. 3. SEM images of samples prepared by physical (S, left) and chemical (PH, right)activation processes.

Table 2
Spectral features of cellulose (C), lignine (L), vine shoot (VS) and chemically activated samples. Temptative assignation. Asterisks (*) denote that the band is present in the FT-IR spectrum.

Cellulose (C), lignine (L) and vine shoot (VS)				
Wavenumbers/cm^{-1}	Assignation	C	L	VS
3500–3300	ν(O–H) (Intermolecular H-bond)	*	*	*
2930–2900	ν (C–H) asymmetric	*	*	*
2855–2850	ν (C–H) symmetric	*	*	*
1740	ν (C=O), esters			*
1712	ν (C=O), aliphatic ketones, carboxylic acids (aliphatic α,β-unsaturated), aromatic esters		*	
1674	ν (C=O), α, β -unsaturated ketones, OH-substituted aromatic esters, quinones		*	
1660	ν (C=O), OH-substituted aromatic acids			
1625–1610	ν (C=C), aromatic		*	*
1520–1510	ν (C=C), lignine aromatic ring		*	*
1450–1420	C–H, asymmetric	*	*	*
1375–1317	C–H, symmetric and asymmetric	*		*
1284–1240	ν (C–O) asymmetric, phenols and aromatic ethers and esters		*	*
1215	ν (C–O), phenols		*	
1165	ν (C–O) asymmetric, aliphatic ethers and tertiary alcohols C–C symmetric		*	
1160	ν (C–O) asymmetric, aliphatic ethers ν (C–O), tertiary alcohols C–C, symmetric ν (C–O–C) asymmetric, pyranose rings	*	*	*
1110	ν (C–O), alcohols	*		*
1060	ν (C–O), alcohols	*	*	
1035	ν (C–O), alcohols	*	*	*
897	β-glucosidic bonds	*		*
884–800	C–H, out-of-plane deformation in aromatic rings		*	*
614	O–H out-of-plane deformation in aromatic rings			*
700–400	ν (C–C)	*	*	*
Chemically activated samples Wavenumbers/cm^{-1}	**Assignation**			
1707	ν (C=O) aliphatic ketones, carboxilic acids			
1625–1425	ν (C=C), skeletal (aromatic rings)			
1244–1063	ν (C–O)			
1154–983	ν (C–O) P–O groups			
1147	ν (C–O)			

regarding the micro- and mesoporosity, the preparation of ACs by chemical activation is strongly influenced by the activating agent.

Mercury intrusion curves for samples C600, C900, A, CD, and S are depicted in Fig. 2, left. When compared with C600, a remarkable development of macroporosity and a decrease in mesoporosity in samples A and S can be observed. Just the opposite behavior is observed in sample CD when compared with C900. These assertions are in good agreement with the larger values of V$_{ma-p}$ of samples A and S (0.82 and 0.71 cm^3 g^{-1}, respectively) than for CD (0.57 cm^3 g^{-1}).

The mercury intrusion curves of samples prepared by chemical

activation are shown in Fig. 2, right. The three ACs differ from each other both in terms of pore volumes and porosity distributions. Although the porosity distribution is rather wide for all samples, the most frequent pore size is larger in the order PA > PH > ZC. On the other hand, the development of mesoporosity is lower in the three ACs. From these results, it becomes evident that the chemical activation of VS with ZnCl$_2$, H$_3$PO$_4$ and KOH makes it possible to prepare ACs that exhibit a wide variety of meso- and macroporous structures. All the above exposed is in good agreement with the data summarized in Table 1.

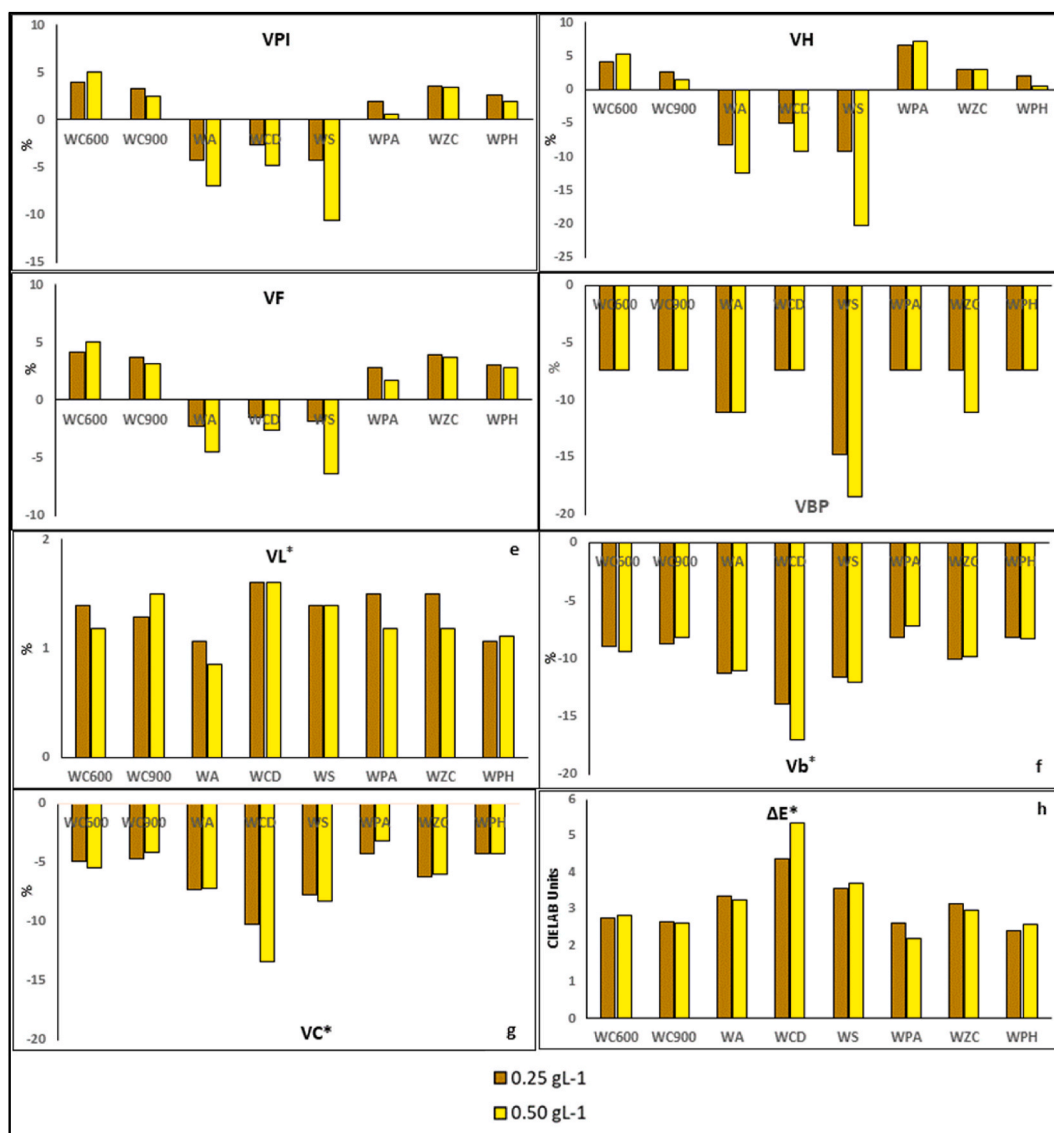The SEM images of two selected adsorbents, namely S and PH,

Fig. 4. Effects of activated carbons (ACs) on the Phenolic Composition and Chromatic characteristics of Pardina control wine (CW). VPI, VH, VF, VBP, VL*, Vb* and VC* are variations (%) of Polyphenol Index, Hydroxycinnamates, Flavonoids, Brown polymers, Lightness, Yellowness and Chromaticity respectively on treated wines respect to control wine. ΔE*: Color differences between wines treated and control wine. WC600 and WC900: wines treated with carbonized at 600 and 900 °C; WCD, WA and WS: Wines treated with carbons prepared by physical activation CD (carbon dioxide), A (air), S (steam) respectively; WPA, WZC and WPH: Wines treated with carbons prepared by chemical activation PA (H_3PO_4), ZC ($ZnCl_2$) and PH (KOH) respectively.

illustrate the morphology of the samples and are shown in Fig. 3. The chemically activated samples exhibit more diversity -in terms of cavities and pore sizes-than ACs obtained by physical activation. In the chemical method, AA is used in solution and must be transferred from the liquid phase to the lignocellulosic substrate. On the contrary, in the physical method, AA is in gaseous phase, which could allow better contact with the solid phase, i.e., with the charred precursor. This, in turn, results in a more homogeneous product.

3.1.2. Surface chemistry

The FT-IR spectrum obtained for VS (Fig. S1a, Supplementary material) reveals the presence of a relatively large number of bands and shoulders that have been assigned as shown in Table 1 (Suárez-García et al., 2002). VS consist mainly of lignin and cellulose. In lignin, cross-linking between molecular fragments through C–O–C and C–C bonds are frequent. The spectral features of VS and the assignation of bands summarized in Table 2 suggest that the most common surface groups in VS are those involving O–H, C=O, C=C, and C–O bonds.

The FT-IR spectra corresponding to the charred and physically activated samples are shown in Fig. S1b. From these spectra, it can be stated that remarkable changes in the chemical composition of the surface take place because of the output of a large amount of volatile matter during the pyrolysis process of VS. Samples C600 and C900 exhibit less surface functional groups and atomic structures than the starting material, VS.

The band centered around 1500 cm^{-1} is attributable to skeletal vibrations in aromatic rings. The FT-IR spectra of the physically activated samples show many absorption bands, which are also relatively strong. It can be assumed that the oxidation of the charred products in the presence of air, CO_2, or steam results in an increase of the functional groups and/or surface structures, particularly for the sample physically activated in air. Table 2 summarizes the assignation of the bands and shoulders that are recorded in the spectra. The band centered around 1700 cm^{-1} is attributable to the stretching vibration of the C=O bond in quinones or carboxylic acids. This band shifts to lower wavenumbers when such a bond is conjugated with olefinic C=C bonds. The higher intensity of this band for sample A suggests the presence of a larger
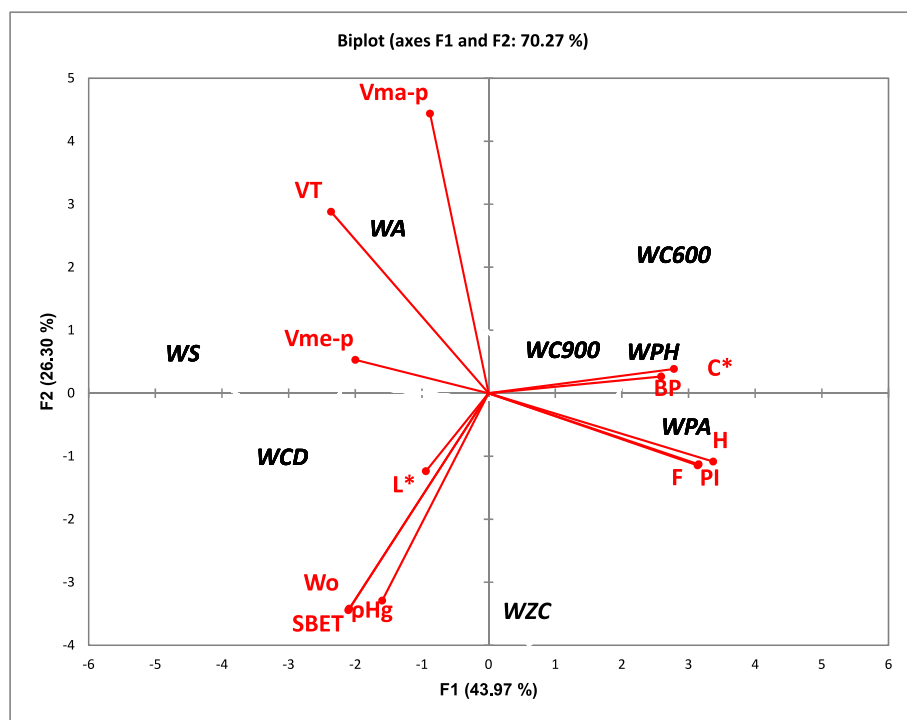
Fig. 5. PCA plot of Pardina wines treated with 0.50 g L^{-1} of ACs and phenolic composition, chromatic characteristics and textural characteristics of ACs as variables. PI, H, F, BP, L*, and C* are Polyphenol Index, Hydroxycinnamates, Flavonoids, Brown polymers, Lightness, and Chromaticity values respectively on treated wines at 0.5 gL^{-1} dose. V_{me-p}, V_T, V_{ma-p}, W_o, S_{BET}, and ρ_{Hg} are mesopore volume, total pore volume, macropore volume, micropore volume, specific surface area, and mercury density of activated carbons, respectively. WC600 and WC900: wines treated with carbonized at 600 and 900 °C; WCD, WA and WS: Wines treated with carbons prepared by physical activation CD (carbon dioxide), A (air), S (steam) respectively; WPA, WZC and WPH: Wines treated with carbons prepared by chemical activation PA (H_3PO_4), ZC ($ZnCl_2$) and PH (KOH) respectively.

concentration of surface oxygen groups. Furthermore, the bands centered at wavenumbers below 1000 cm^{-1} are attributable to vibrations of C–H bonds in aromatic rings. The spectral position of these bands varies with the degree of substitution of the aromatic ring.

Finally, the FT-IR spectra of the chemically activated samples are shown in Fig. S1c. The bands recorded in the infrared region are assignable to vibrational modes of bonds present in functional groups and surface carbon structures. The most remarkable spectral features are also listed in Table 2. Two particularly intense bands appear centered around 1600 and 1150 cm^{-1}. Such bands can be assigned to C–O bond vibrations in alcohol and ether groups.

The pH$_{PZC}$ values are listed in Table 1. In general, C600, C900 and the samples prepared by the method of physical activation possess a basic pH$_{PZC}$, ranging from 8.6 up to 10.0. This is attributable to C=O bonds in different surface groups (e.g., pyrone) but also to π-electrons located in graphene layers, heteroatoms (e.g., N), inorganic impurities, etc. (Montes-Morán et al., 2004). For the three ACs prepared by the chemical activation method, the pH$_{PZC}$ is below 7.0, indicating the acidic character of the surface of these samples. It is noteworthy the low value of pH$_{PZC}$ (2.0) of the PA sample.

3.2. Effect of the activated carbons on the wine. Influence of their physico-chemical and textural characteristics

3.2.1. Phenolic composition and chromatic characteristics

Polyphenols exert a noticeable influence in the color and flavor of wines (Natolino & Celotti, 2022). Fig. 4 a, b, and c show the variations of the values of the polyphenols index, hydroxycinnamates and flavonoids (VPI, VH, and VF) compared to control wine (CW), in the treated wines WC600, WC900, WA, WCD, WS, WPA, WZC, and WPH obtained after treatments with samples C600, C900, A, CD, S, PA, ZC, and PH, respectively at doses of 0.25 and 0.50 g L^{-1}. At both doses, the effect of ACs on these parameters depended mainly on the used carbon. Decreases of these parameters were registered for WA, WCD and WS. When the extent of variation was calculated, the sequence WS > WA > WCD was always observed, except for VF at 0.25 g L^{-1}, which followed the order WA > WS > WCD. Also, a certain correspondence between the

dose of carbon added and the range of the variation was registered since VPI, VH, and VF were higher (1.5–2 times) at a dose of 0.50 g L^{-1} than for 0.25 g L^{-1}. Concerning the effect of three ACs on these parameters, it was observed that VH > VPI > VF regardless of what the dose was.

The brown pigments (BP) result from the oxidation of the phenolic compounds initially present in the wine; they are responsible for the browning of white wines and cause declines in their visual and global organoleptic evaluation (Cosme et al., 2012). Values of BP were lower in all treated wines than in control wine, and VBP had negative values in all cases. The decreases depended on the added AC and it was similar for both doses. The most effective AC to remove brown pigments from the Pardina wine was S, as suggested by the values of VBP in WS at a dose of 0.25 g L^{-1} (i.e., −13) and 0.50 g L^{-1} (−17).

The values of VL*, Vb*, and VC* are shown in Fig. 4 e, f, and g, respectively. Clearly, the chromatic characteristics of the Pardina wine were modified after contact with the ACs. All ACs increased L* and decreased b* and, consequently, C*. The increase in L* is attributable to the removal of pigments present in the control wine and denotes that the wine changed towards higher transparency. Since C* is a combination of a* and b*, this parameter also changed because of the discoloring process.

The incidence of the treatments with the ACs was more noticeable for b* than for a* (results not shown). Fig. 4 f reveals a reduction in b* (i.e., yellow color) after treatment with all the ACs. The greatest Vb* was registered for WCD, while very similar values were achieved for WS and WA, and the smallest variations correspond to WPH. Similar results were found for VC* (Fig. 4 g).

To assess the discoloring capacity of ACs, the colorimetric differences (ΔE*) between the control wine and the treated wines were calculated. According to Fig. 1h, the highest values were found for WCD (ΔE* = 4.36 and 5.34 CIELAB units for doses of 0.25 g L^{-1} and 0.50 g L^{-1}, respectively). According to the investigations of Martinez et al. (2016), 2.7 units of CIELAB is the threshold value of this parameter for the human eye to detect color differences between wines. Thus, untrained tasters would be able to adequately differentiate WA, WCD, WS, and WZC from CW by comparing their color. Correlation analysis (Pearson's correlation) was performed between the values of textural

Table 3
Influence of activated carbons (ACs) on the volatile composition and aromatic characteristics of Pardina control wine (CW).

Compound	Volatile composition (µg L^{-1})					Odor Threshold (µg L^{-1})	Odor descriptor	OAV				
	CW	Dose 0.25 g L^{-1}		Dose 0.50 g L^{-1}				CW	Dose 0.25 g L^{-1}		Dose 0.50 g L^{-1}	
		WCD	WS	WCD	WS				WCD	WS	WCD	WS
1-hexanol	273.97	330.76	319.75	339.60	353.81	8000	Vegetable, grass	<1	<1	<1	<1	<1
(Z)-3-hexen-1-ol	37.80	53.13	49.04	53.96	55.61	400	Cut grass	<1	<1	<1	<1	<1
Total C6 compounds	**311.76**	**383.90**	**368.79**	**393.55**	**409.42**							
1-propanol	147.83^b	219.84^b	221.77^b	217.96^b	258.98^a	750,000		<1	<1	<1	<1	<1
2-methyl-1-propanol	194.47	319.17	292.51	319.94	377.44	65,000	Alcohol, banana, solvent	<1	<1	<1	<1	<1
1- butanol	35.14	32.02	37.85	41.08	58.66	150,000	Alcohol fusel	<1	<1	<1	<1	<1
3-methyl-1-butanol	8234.08	13350.00	11890.37	13293.88	15072.00			<1	<1	<1	<1	<1
3-methyl-1-pentanol	26.92	38.86	31.60	37.73	39.29			<1	<1	<1	<1	<1
2-phenyletanol	5226.72	6699.63	6186.08	6360.92	6730.21	10,000	Rose, sweetish	<1	<1	<1	<1	<1
Total Alcohols	**13865.16**	**20659.52**	**18660.18**	**20271.51**	**22536.68**							
Ethyl butyrate	294.08	271.29	301.91	287.86	309.65	20	Papaya, butter, sweetish	14.70	13.56	15.10	14.39	15.48
Ethyl hexanoate	984.48^a	720.70^b	778.50^{ab}	645.58^b	596.69^b	14	Apple, fruity, sweetish	70.32^a	51.48^b	55.61^b	46.11^b	42.62^b
Ethyl octanoate	703.47^a	320.86^b	322.59^b	235.65^{bc}	178.08^c	5	Apple, sweetish	140.69^a	64.17^b	64.52^b	47.13^{bc}	35.62^c
Ethyl decanoate	77.95^a	26.64^b	23.21^b	14.23^b	12.34^b	200	Apple, fruity, solvent	<1	<1	<1	<1	<1
Ethyl lactate	253.85	399.14	356.20	396.57	447.54	154,700	Strawberry, raspberry	<1	<1	<1	<1	<1
Diethyl succinate	387.42	375.88	454.84	441.43	455.92	120,000		<1	<1	<1	<1	<1
Diethyl malate	193.14	255.47	238.26	254.72	268.50	10,000		<1	<1	<1	<1	<1
Total Ethyl esters	**2894.39**	**2369.98**	**2475.51**	**2276.04**	**2268.72**							
Hexyl acetate	146.73^a	103.66^{bc}	106.55^b	85.22^{bc}	72.53^c	670	Sweetish, perfumed	<1	<1	<1	<1	<1
3-methylbutyl acetate	2646.81	2384.78	2722.06	2473.35	2463.11	30	Banana, Apple, estery	88.23	79.49	90.74	82.44	82.10
2-phenylethyl acetate	301.81^a	175.79^{bc}	187.97^b	129.67^b	116.73^c	250	Rose, honey, tobacco	1.21^a	0.70^{bc}	0.75^b	0.52^b	0.47^c
Total Acetates	**3095.35**	**2664.23**	**3016.58**	**2688.24**	**2652.37**							
2 + 3 methylbutyrate	12.79	17.69	20.81	18.13	21.97	34	Cheese, old hops, sweaty	<1	<1	<1	<1	<1
Butyric acid	18.42	25.98	25.24	26.74	32.98	173	Rancid, cheese	<1	<1		<1	<1
Hexanoic acid	1534.11	1988.29	1904.31	2037.04	2099.52	30	Geranium, vegetable	51.14	66.28	63.48	67.90	69.98
Octanoic acid	6123.29^a	4605.15^{bc}	4856.65^{ab}	3776.39^{bc}	3363.22^c	500	Sweet, cheese	12.25^a	9.21^{bc}	9.71^{ab}	7.55^{bc}	6.73c
Decanoic acid	555.10^a	206.45^{bc}	212.68^b	87.94^d	133.31^{cd}	1000	Rancid, fat	<1	<1	<1	<1	<1
Hexadecanoic acid	64.62	139.42	102.38	134.20	90.53	6100	Soapy, waxy	<1	<1	<1	<1	<1
Total Volatile fatty acids	**8308.33**	**6982.98**	**7122.07**	**5992.50**	**5608.22**							
4-vinylguaiacol	82.16^a	54.07^{ab}	42.13^b	27.28^b	35.07^b	10.00	Clove, curry	8.22^a	5.41^{ab}	4.21^b	2.73^b	3.51^b
4-vinylphenol	30.55^a	10.78^{ab}	17.83^{ab}	0^b	0^b	180.00	Stramonium, almond shell	<1	<1	<1	<1	<1
Total Volatile phenols	**112.71**	**64.85**	**59.97**	**27.28**	**35.07**							
β-damascenone	7.50	4.88	8.33	10.22	5.92	0.05	Rose, honey	150.09	97.55	166.63	204.30	118.30
γ-butyrolactone	122.96^b	173.41^{ab}	204.60^{ab}	227.44^{ab}	251.81^a	20,000		<1	<1	<1	<1	<1

CW: control wine. WCD and WS: Wines treated with carbons prepared by physical activation: CD (carbon dioxide), S (steam). For a given compound, lowercase letters in superscript indicate statistically significant differences between treatments (p≤0.05).

characteristics of the ACs and the corresponding values of PI, H, F, BP, L*, and C* obtained in treated wines at doses of 0.50 g L^{-1} (Table S2, Supplementary material). Significant correlations were found between the values of V$_T$ and PI (r^2 = −0.557), H (r^2 = -0.679), and F (r^2 = −0.56). Also, V$_{me-p}$ was correlated with L* (r^2 = 0.63) and C*(r^2 = −0.55). Therefore, it can be concluded that V$_T$ and V$_{me-p}$ are the main factors related with the effectiveness of ACs when applied to the elimination of phenolic substances and discoloration of the white wine under study.

Principal component analysis (PCA) was used to classify the different wines treated with adsorbent doses of 0.50 g L^{-1} in terms of their phenolic composition and chromatic characteristics (Fig. 5). The first axis (F1) explained 43.97% of the variability, whereas the second axis (F2) explained 26.30%. Hence, both axes together explain 70.27% of the variability.

The positive F1 was strongly correlated with PI, H, F, C*, and BP. This axis separated the wines WS, WCD, and WA (that are in the negative region of the F1 axis) from the remaining ones. According to the PCA plot, the wines that were treated with the ACs exhibiting the largest values of V$_T$ and V$_{me-p}$ (i.e., S and CD) presented the lowest values of phenolic substances and chromatic parameters. The results show that the ACs with the highest values of V$_T$ and a well-developed porosity, specifically in the region of the macro- and mesopores, were the most effective in eliminating phenolic substances and therefore are the most promising candidates to be used in the winemaking industry. These results confirm the previous investigations of Corcho-Corral et al. (2005), who showed the suitability of ACs made from VSs to discoloring the white wines cv. Cayetana, cv. Macabeo and cv. Sauvignon Blanc from Extremadura (Spain).

3.2.2. Volatile composition and aromatic characteristics

Table 3 shows the volatile compounds identified and quantified in Pardina wines grouped in eight chemical families: C6 compounds, alcohols, ethyl esters, acetates, volatile fatty acids, volatile phenols, C13-norisoprenoid (β-damascenone) and lactone (γ-butyrolactone). Table 3 also shows the odor descriptor, odor threshold, and OAV for each of the compounds that were quantified. The results show 29 volatile compounds identified and quantified. However, only nine compounds (∼30%) showed an impact on the wine aroma, i.e., exhibited concentrations above their odor threshold (OAV>1).

Only the compounds with OAV greater than 1 contribute individually to the wine aroma and can be perceived (Lu et al., 2020). As in other white wines, alcohols are the most abundant chemical family of the volatiles in Pardina wines (Sánchez-Palomo et al., 2017). Alcohols are represented by seven compounds, where the highest concentration corresponded to isoamyl alcohol (3-methyl-1-butanol) followed by 2-phenylethanol. However, these compounds did not exhibit any influence on wine aroma (OAV<1). Among volatile fatty acids and acetates, octanoic acid, hexanoic acid, and 3-methylbutylacetate showed the highest concentrations and exerted the most remarkable influence on wine aroma. Three ethyl esters (namely, ethyl butyrate, ethyl hexanoate, and ethyl octanoate) also showed an impact in wine aroma (Gómez García-Carpintero et al., 2014; Mihnea et al., 2015). Medium-chain fatty acid esters and acetates contribute favorably to wine aroma increasing the intensities of sweet fruity and acid fruity flavours (Ma et al., 2017).

Among volatile phenols, represented by two compounds, only 4-vinylguaiacol (clove and curry aromas) shows OAV>1. C13-norisoprenoids group was represented by only one compound, β-damascenone (rose and raisin aroma) (Ferrero-del-Teso et al., 2020), although in a very low concentration. Nevertheless, it was the compound with the highest impact in wine aroma because of its lower odor threshold (OAV between 97.55 and 150.09). Therefore, these results show that β-damascenone was the most potent odorant substance in Pardina white wine.

The presence of volatile compounds that are generated in the successive steps of winemaking can be fined through several additives (Almeida Santos et al., 2020). In this work, regarding volatile concentration, eleven compounds were affected by the contact of CW with the ACs. Overall, the use of S and CD samples resulted in a decrease in the concentration of these compounds. Only 1-propanol and γ-butyrolactone increased their concentration when sample S was kept in contact with Pardina wine, mainly at a high dose (0.50 g L^{-1}).

Among the volatile compounds with impact in the wine aroma (OAV>1), only five of them were influenced by the contact with ACs. In general, the values of the volatile compounds on WS and WCD indicate that S and CD carbons exerted a similar effect. Decreases were found in ethyl hexanoate, ethyl octanoate, 2-phenylethyl acetate, octanoic acid, and 4-vinylguaiacol when S and CD carbons were applied to the wine. The ethyl octanoate was severely affected (62.4% average decrease of OAV), whereas 2-phenylethyl acetate, octanoic acid and ethyl hexanoate were less affected by the application of ACs.

In all cases, significant decreases of volatile phenols, especially 4-vinylphenol, were observed. Because of their low olfaction thresholds, these substances provide unpleasant aromas to the wines that can be perceived even at low concentrations in wines (Table 3). Vinylphenols can hide fruity aromas on white and rosé wines, and the freshness desirable in this type of wine decreases (Chatonnet et al., 1993). The removal of these substances could reduce the negative impact caused by the decrease in the intensity of sweetish, fruity and apple aroma due to the adsorption of ethyl octanoate by the ACs. These findings extend the implementation of ACs prepared in the enology industry. Filipe-Ribeiro et al. (2017) reported similar results when several ACs were added to a red wine from Douro Valley. According to these researchers, regardless of the carbon used, esters and acids were the compounds most affected by the treatment.

4. Conclusions

From the results obtained in this work, the following conclusions may be drawn:

- Activated carbons with a broad spectrum of surface, textural, and chemical properties have been obtained. As a rule, the ACs prepared from VSs exhibit a low degree of microporosity development. As for the meso- and macroporosity, the pore volumes are quite high, especially for the ACs prepared by the physical activation method.
- Activated carbons differ markedly in the acid-base character of their surface. ACs prepared by the chemical activation method are mainly acidic, whereas those physically activated are basic. Thus, the pH$_{PZC}$ decreases according to the sequence: CD (10.0) = S (10.0) > A (8.6) > PH (6.4) > ZC (3.4) > PA (2.0).
- Activated carbons prepared by physical activation efficiently adsorb polyphenolic compounds responsible for browning of white wines and can remove vinylphenols, volatile substances which provide unpleasant aroma and decrease the intensity of sweetish, fruity and apple aroma of white and roses wine. Consequently, it can be stated that ACs with promising applications in enology industry can be prepared from a cheap and abundant waste such as VSs.

Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2022.113601.

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